

**GLYCOLISED COPOLYESTER-BASED STRUCTURE FOR MANUFACTURING
TRANSPARENT HOLLOW BODIES BY COEXTRUSION BLOW-MOLDING**

5

*_*_*_*_*_*_*_*_*_*

The present invention relates to a multilayer structure comprising a coextrusion tie layer adhering to a layer of glycolised polyester copolymer. The said tie comprises a blend of metallocene polyethylene, abbreviated as PEm in the text herein below, non-metallocene LLDPE, both of which are co-grafted, and non-grafted polyethylene. The invention also relates to articles comprising such a structure, in particular hollow bodies.

In the current state of the art of coextrusion blow-molding, it is possible to obtain bottles with gas-barrier properties with structures comprising polypropylene layers, but these bottles are not sufficiently transparent. It is possible to obtain via another two-step process (a step of coinjection of preforms followed by a step of biaxial-drawing blow-molding) bottles with barrier properties manufactured with the aid of a multilayer structure comprising at least one polyester layer and at least one EVOH or PA-based layer, but in this case the cohesion of the structure is not very good since the adhesion between the polyester layer and the barrier layer is low.

Document FR 2806734 from the Applicant discloses a composition comprising metallocene PE and non-metallocene LLDPE co-grafted with unsaturated carboxylic acid or a derivative thereof, the said composition being diluted in PE or an elastomer. The PE in the said patent application may be a PE homopolymer or copolymer with, in this case, an α -olefin as comonomer, and it may be a PE such as an HDPE (high-density PE), LDPE (low-density PE), LLDPE (linear low-density PE) or VLDPE (very-low-density PE) or a metallocene PE.

The technical problem consists in manufacturing an article, in particular a bottle, which has good transparency and gas-barrier qualities, given that the prior-art solutions are at the present time unsatisfactory.

The Applicant has now found that it is possible to obtain, by extrusion blow-molding, hollow bodies with high transparency accompanied by gloss, combined with high impermeability to gases and having good mechanical properties, by using structures of the glycolised polyester copolymer/tie/EVOH type.

5 The tie, used in the invention, thus allows the production of varied structures comprising, inter alia, a tie layer, a glycolised copolyester layer and a layer of barrier material.

These structures are useful for manufacturing packagings or flexible or rigid hollow bodies such as sachets, bottles or containers, or for manufacturing coextruded
10 pipes, tubes, films and sheets.

The invention concerns a process for manufacturing a transparent article with gas-barrier properties by coextrusion blow-molding, the said article comprising at least a structure of the type: layer of EVOH/tie layer/layer of glycolised copolyester.

According to one embodiment, the said article comprises at least a structure of the
15 type: layer of EVOH/tie layer/layer of PETG as glycolised copolyester.

According to one embodiment, the tie is a composition comprising at least a PE homopolymer or copolymer grafted with a grafting monomer chosen from unsaturated carboxylic acids and derivatives thereof.

The invention concerns also a multilayer structure comprising at least:

- 20 ▪ one layer of coextrusion tie (L) comprising:
- 5% to 35 % by weight of a polymer (A) which itself consists of a blend of 80% to 20% by weight of a metallocene polyethylene (A1) with a density of between 0.863 and 0.915 and from 20% to 80% by weight of a non-metallocene LLDPE polyethylene (A2) with a density of between 0.900 and 0.950, the blend of polymers
25 (A1) and (A2) being co-grafted with a grafting monomer chosen from unsaturated carboxylic acids and derivatives thereof, the content of the grafting monomer in the said blend being between 30 and 100 000 ppm and preferably between 600 and 5000 ppm:
 - 95% to 65% by weight of polyethylene homopolymer or copolymer (B), the comonomer of which contains 3 to 20 carbon atoms and preferably 4 to 8 carbon atoms,
30 the MFI, melt flow index measured under 2.16 kg at 190°C according to ASTM

standard D1238, of which is between 0.5 and 30 and preferably between 3 and 15 g/10 minutes;

the total being 100%, the blend of (A) and (B) being such that its MFI is between 0.1 and 15 and preferably between 1 and 13 g/10 minutes;

- 5 ▪ one layer of glycolised polyester copolymer (E).

According to one embodiment, the glycolised polyester copolymer is PETG.

According to one embodiment, the structure also comprises a layer of barrier material (F).

10 According to one embodiment, the structure is characterized in that the layer of barrier material is a layer of EVOH.

The invention is relating to an article comprising a structure above mentioned.

According to one embodiment, the article is characterized in that it is a bottle, a hollow body or a container.

The invention will now be described in detail.

15 As regards (A1), the term "metallocene polyethylene" denotes the polymers obtained by copolymerization of ethylene and of α -olefin containing from 3 to 30 carbon atoms and preferably from 3 to 8 carbon atoms, for instance propylene, butene, pentene, hexene or octene in the presence of a single-site catalyst.

20 Examples of α -olefins containing 3 to 30 carbon atoms, as possible comonomers, include propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-tetracosene, 1-hexacosene, 1-octacosene and 1-triacontene. These α -olefins may be used alone or as a mixture of two or more than two.

25 A single-site catalyst generally consists of a metal atom, which may be, for example, zirconium or titanium, and of two cycloalkyl molecules linked to the metal. More specifically, metallocene catalysts are usually compounds of two cyclopentadiene rings linked to the metal. These catalysts are frequently used with aluminoxanes as co-catalysts or activators, preferably methylaluminoxane (MAO). Hafnium may also be
30 used as the metal to which the cyclopentadiene is attached. Other metallocenes may

include transition metals from groups IV A, V A, and VI A. Metals of the lanthanide series may also be used.

These metallocene polyethylenes may also be characterized by their $\overline{Mw}/\overline{Mn}$ ratio < 3 and preferably < 2 in which \overline{Mw} and \overline{Mn} denote, respectively, the weight-average molar mass and the number-average molar mass. The term "metallocene polyethylene" also denotes those with an MFR (Melt Flow Ratio) of less than 6.53 and an $\overline{Mw}/\overline{Mn}$ ratio of greater than MFR minus 4.63. MFR denotes the ratio of the MFI₁₀ (MFI under a 10 kg load) to the MFI₂ (MFI under a 2.16 kg load). Other metallocene polyethylenes are defined by an MFR of greater than or equal to 6.13 and an $\overline{Mw}/\overline{Mn}$ ratio of less than or equal to MFR minus 4.63.

The density of (A1) is advantageously between 0.863 and 0.915. The MFI of the PEM (A1) is between 0.5 and 30 g/10 minutes (according to ASTM Standard D1238 at 190°C under 2.16 kg).

As regards (A2), the polymer (A2) is a copolymer of ethylene and of an α -olefin of LLDPE (linear low-density polyethylene) type and is not of metallocene type. α -Olefins advantageously contain from 3 to 30 carbon atoms. The list of these α -olefins has already been given above. They are preferably α -olefins containing from 3 to 8 carbon atoms.

The density of (A2) is advantageously between 0.900 and 0.950.

The MFI, or melt flow index, of (A2) is between 0.1 and 8 g/10 minutes (according to ASTM Standard D1238 at 190°C under 2.16 kg).

The blend of polymers (A1) and (A2) is grafted with a grafting monomer, i.e. the polymers (A1) and (A2) are co-grafted. The grafting monomer is chosen from unsaturated carboxylic acids or functional derivatives thereof.

Examples of unsaturated carboxylic acids are those containing 2 to 20 carbon atoms, such as acrylic acids, methacrylic acids, maleic acid, fumaric acid and itaconic acid. The functional derivatives of these unsaturated carboxylic acids comprise anhydrides, ester derivatives, amide derivatives, imide derivatives and metal salts (such as alkali metal salts) of these unsaturated carboxylic acids.

Unsaturated dicarboxylic acids containing 4 to 10 carbon atoms and functional derivatives thereof, particularly the anhydrides thereof, are grafting monomers that are particularly preferred.

These grafting monomers comprise, for example, maleic acid, fumaric acid, itaconic acid, citraconic acid, allylsuccinic acid, cyclohex-4-ene-1,2-dicarboxylic acid, 4-methylcyclohex-4-ene-1,2-dicarboxylic acid, bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid and x-methylbicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid and the functional derivatives thereof, and maleic anhydride, itaconic anhydride, citraconic anhydride, allylsuccinic anhydride, cyclohex-4-ene-1,2-dicarboxylic acid, 4-methylenecyclohex-4-ene-1,2-dicarboxylic anhydride, bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic anhydride and x-methylbicyclo(2,2,1)hept-5-ene-2,2-dicarboxylic anhydride.

Examples of other grafting monomers comprise C₁-C₈ alkyl esters or glycidyl ester derivatives of unsaturated carboxylic acids, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylate, monoethyl maleate, diethyl maleate, monomethyl fumarate, dimethyl fumarate, monomethyl itaconate and diethyl itaconate; amide derivatives of unsaturated carboxylic acids, such as acrylamide, methacrylamide, maleic monoamide, maleic diamide, maleic N-monoethylamide, maleic N,N-diethylamide, maleic N-monobutylamide, maleic N,N-dibutylamide, fumaric monoamide, fumaric diamide, fumaric N-monoethylamide, fumaric N,N-diethylamide, fumaric N-monobutylamide and fumaric N,N-dibutylamide; imide derivatives of unsaturated carboxylic acids, such as maleimide, N-butylmaleimide and N-phenylmaleimide ; and metal salts of unsaturated carboxylic acids, such as sodium acrylate, sodium methacrylate, potassium acrylate, and potassium methacrylate. Maleic anhydride is preferred.

Various known processes may be used to graft a grafting monomer onto the blend of polymer (A1) and (A2). The blend may contain the additives usually used in the implementation of polyolefins, in contents of between 10 ppm and 50 000 ppm, such as antioxidants based on substituted phenolic molecules, UV stabilizers,

processing agents such as fatty amides, stearic acid and its salts, fluoropolymers known as agents for preventing extrusion defects, amine-based anti-misting agents, anti-blocking agents such as silica or talc, masterbatches with dyes and nucleating agents, inter alia.

5 For example, grafting may be performed by heating the polymers (A1) and (A2) to elevated temperature, about 150°C to about 300°C, in the presence or absence of a solvent, with or without a free-radical initiator. Suitable solvents that may be used in this reaction are benzene, toluene, xylene, chlorobenzene and cumene, inter alia. Suitable free-radical initiators that may be used include t-butyl hydroperoxide, cumene
10 hydroperoxide, diisopropylbenzene hydroperoxide, di-t-butyl peroxide, t-butylcumyl peroxide, dicumyl peroxide, 1,3-bis(t-butylperoxyisopropyl)benzene, acetyl peroxide, benzoyl peroxide, isobutyryl peroxide, bis(3,5,5-trimethylhexanoyl) peroxide and methyl ethyl ketone peroxide.

 In the blend of polymers (A1) and (A2) modified by grafting, obtained in the
15 abovementioned manner, the amount of the grafting monomer may be chosen in an appropriate manner but is preferably from 0.01 to 10% by weight, i.e. preferably from 600 ppm to 5000 ppm, relative to the weight of the co-grafted (A1) and (A2).

 The amount of the grafted monomer is determined by assaying the succinic functions by FTIR spectroscopy. The MFI, or the melt flow index, of (A), i.e. of the
20 blend of (A1) and (A2) that have been co-grafted, is between 0.1 and 15 g/10 minutes (ASTM D 1238-190°C-2.16 kg), advantageously between 0.1 and 5 g/10 minutes and preferably between 0.1 and 3 g/10 minutes.

 As regards the polyethylene (B), it is a polyethylene homopolymer or it may be chosen from copolymers of ethylene with a monomer chosen from α -olefins,
25 unsaturated carboxylic acid esters and vinyl esters of saturated carboxylic acids. The α -olefins have been defined above. The unsaturated carboxylic acid esters are, for example, alkyl (meth)acrylates in which the alkyl contains from 1 to 24 carbon atoms. Examples of alkyl acrylates or methacrylates that may be used are especially methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl
30 acrylate. The vinyl esters of saturated carboxylic acids are, for example, vinyl acetate or

vinyl propionate. (B) may be an HDPE, LDPE, LLDPE or VLDPE polyethylene or a metallocene.

The polymer (B) may also be a polymer of elastomeric nature, i.e. it may be (i) an elastomer within the meaning of ASTM D412, i.e. a material that can be drawn at room temperature to twice its width, maintained in this state for 5 minutes and then, when it is released, it returns to within 10% of its initial length, or (ii) a polymer that does not have exactly the above characteristics, but that can be drawn and return to substantially its initial length. Examples that may be mentioned include:

- EPRs (ethylene-propylene rubber also denoted as EPM) and EPDMs (ethylene-propylene-diene),
- styrene elastomers, such as SBR (styrene-butadiene-rubber), styrene-butadiene-styrene (SBS) block copolymers, styrene-ethylene/butene/styrene (SEBS) block copolymers and styrene-isoprene-styrene (SIS) block copolymers.

Advantageously, (B) is an LLDPE with a density between 0.910 and 0.935, an HDPE with a density between 0.935 and 0.950 or a polyethylene of metallocene type with a density between 0.863 and 0.915.

The multilayer structure of the present invention comprises a layer (L) comprising the tie described above and a layer (E) directly attached to a first side of the said layer (L). The layer (E) is a layer of glycolised polyester, advantageously a glycol-modified polyethylene terephthalate and more preferably PETG (poly)ethylene-co-1,4-cyclohexanedimethyleneterephthalate.

A layer (F) may also be directly attached to the second side of the layer (L), the layer (L) being sandwiched between the layers (E) and (F), the said layer (F) being either a layer of polymer chosen from the group of polyamides and saponified copolymers of ethylene and of vinyl acetate (EVOH).

However, the multilayer structure may also comprise a layer (L) comprising the tie sandwiched between two layers (F).

The following structures may be listed by way of example: PA denoting the polyamide, L the tie, PE the polyethylene, PETG [(poly)ethylene-co-1,4-

cyclohexanedimethyleneterephthalate] the glycolised copolyester and EVOH the saponified copolymer of ethylene and of vinyl acetate:

- Structures of (E) layer / (L) layer / (F) layer type: PE/L/EVOH/L/PETG
- Structures of (E) / (L) layer / (E) layer and (F) layer / (L) layer / (F) layer type: PETG/L/PE, PETG/L/PETG

5

More specifically, the polyamides are synthetic with a long chain containing structural units of the amide group in the main chain, such as PA-6, PA-6,6, PA-6,10, PA-11, PA-6/6,6 and PA-12.

10 Saponified copolymers of ethylene and of vinyl acetate have a degree of saponification of about 90 mol% to 100 mol% and are obtained by saponifying an ethylene/vinyl acetate copolymer having an ethylene content of about from 15 mol% to about 60 mol%.

15 The glycolised polyesters are glycolised copolymers. Suitable glycolised copolyesters that are useful in the invention may be formed from aromatic dicarboxylic acids, from dicarboxylic acid esters, from dicarboxylic ester anhydrides and from glycols, or mixtures thereof.

20 Partially aromatic copolyesters formed from repeating units comprising terephthalic acid, dimethyl terephthalate, isophthalic acid, dimethyl isophthalate, dimethyl 2,6-naphthalenedicarboxylate, 2,6-naphthalenedicarboxylic acid, 1,2-, 1,3- and 1,4-phenylene dioxidoacetic acids, ethylene glycol, diethylene glycol, 1,4-cyclohexanedimethanol and 1,4-butanediol, or mixtures thereof, are also suitable.

For the diacid component, the structure of the polyesters preferably comprises repeating units comprising terephthalic acid, dimethyl terephthalate, isophthalic acid, dimethyl isophthalate, dimethyl 1,4-cyclohexanedicarboxylate and/or dimethyl 2,6-naphthalenedicarboxylate. The dicarboxylic acid of the polyester may be modified with one or more different dicarboxylic acids (preferably up to about 20 mol%). Such dicarboxylic acids comprise aromatic dicarboxylic acids preferably containing 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably containing 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably containing 8 to 12 carbon atoms.

25

30 Examples of dicarboxylic acids are: terephthalic acid, phthalic acid, isophthalic acid,

naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid and sebacic acid, or mixtures thereof.

For the glycol component, the preferred glycols include ethylene glycol, diethylene glycol, neopentyl glycol, 1,4-cyclohexanedimethanol, and mixtures thereof. More preferably, the glycol residue component is from about 10 to 100 mole percent 1,4-cyclohexanedimethanol and from about 90 to 0 mole percent ethylene glycol. Furthermore, the glycol may be modified with one or more diols (preferably up to about 20 mol %). Such diols comprise: cycloaliphatic diols preferably containing 6 to 20 carbon atoms or aliphatic diols preferably containing 2 to 20 carbon atoms. Examples of such diols comprise: ethylene glycol, diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-2,4-pentanediol, 2-methyl-1,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,3-hexanediol, 1,4-bis(hydroxyethoxy)benzene, 2,2-bis(4-hydroxycyclohexyl)propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis(3-hydroxyethoxyphenyl)propane, 2-bis(4-hydroxypropoxyphenyl)propane and hydroxyethylresorcinol, or mixtures thereof. The glycolised polyesters may be prepared with two or more than two of the above diols.

In addition, the glycolised copolyesters of this invention may include branching agents such as trimellitic acid, trimellitic anhydride, pyromellitic dianhydride, trimethylolpropane, glycerol, pentaerythritol, and the like.

Advantageously, the glycolised polyester is formed from terephthalic acid, ethylene glycol and another diol such as defined above. More preferably, the glycolised polyester is PETG [(poly)ethylene-co-1,4-cyclohexanedimethyleneterephthalate] which is formed from terephthalic acid, ethylene glycol and 1,4-cyclohexanedimethanol.

The inherent viscosity of the glycolised copolyesters generally ranges from about 0.4 to about 1.5 dL/g, preferably about 0.6 to about 1.2 dL/g. Inherent viscosity (I.V.) as used herein refers to determinations made at 25°C using 0.25 gram of polymer

per 100 mL of a solvent composed of 60 weight percent phenol and 40 weight percent tetrachloroethane.

The compositions forming the various layers of the structures of the invention may contain additives such as fillers, stabilizers, glidants, antistatic agents and flame
5 retardants.

The structures of the invention are manufactured by the known process of coextrusion blow-molding.

Table 1 below collates the composition of the ties of Examples 1 to 3.

Table 2 below collates the peel forces F in N/15 mm at various interfaces.

10 The peel tests were performed using the so-called T peel test at a temperature T of 25°C and at a peel rate of 200 mm/minute.

Haze values measured on samples cutted in glycolised copolyester based containers from examples 1 to 3 and polypropylene based container from comparative example 4 are collected in **Table 3**.

15 The containers of the present invention have good transparency, which is characterized by a low haze value, less than 20%, advantageously less than 15% and more advantageously less than 13%. A haze value is defined as the percent of total light which, in passing through the specimen, deviates through forward scatter by more than 0.044 red (2.5°) on the average. The preferred test to obtain the haze value of the bottle
20 is ASTM Method D-1003 as defined in the 1995 Annual Book of ASTM 10 Standards, Volume 8.01.

In the examples 1 to 3, 5-layers containers were made by a coextrusion blow molding process using a BEKUM with 5 extruders equipment. The layers I and V were made from a glycolised copolyester extruded in two single screw extruders of
25 respectively 50mm and 38mm diameter. The layers II and IV were made from tie layer material and extruded in two single screw extruder of 20mm diameter. Layer III was made from EVOH and extruded in a single screw of 30mm diameter. The five layers were extruded together in a coextrusion annular die having a final temperature of 220°C to form a continuous tube (called parison). Then pressurized air was used to expand the
30 hot preform and press it against a female mold cavity to form the container. The

pressure was held until the materials were cooled. The layers **I and V** were made from a glycolised copolyester (50 mole % of copolymer of terephthalate residues with 25 mole % of 1,4-cyclohexanedimethanol and 25 mole % of ethylene glycol and with an inherent viscosity (I.V.) of 0,76 dL/g). The layer III was made from EVOH (SOARNOL DT 2903 from Nippon Gohsei). The layers II and IV were made from ties (L) defined below.

In the comparative example 4, 5-layers container was made by a coextrusion blow molding process using the same process as those used in examples 1 to 3. The layers **I and V** were made from Polypropylene (ATOFINA POLYPROPYLENE PPM R020). The layer III was made from EVOH (SOARNOL DT 2903 from Nippon Gohsei). The layers II and IV were made from tie layer OREVAC PPC from ATOFINA.

The specimens used for peeling tests were cut from coextruded hollow bodies consisting of 5 layers (layers I to V), obtained by coextrusion blow-molding: layer (I) of glycolised copolyester / layer (II) of Tie (L) / layer (III) of EVOH / layer (IV) of tie (L) / layer (V) of glycolised copolyester, with respective thicknesses of layer (I) to layer (V), in μm , of 385/19/41/19/153 for case 1, 470/25/51/17/175 for case 2 and 548/25/56/20/210 for case 3.

The specimen used for comparative example 4 was cut from coextruded hollow bodies consisting of 5 layers (layers I to V), obtained by coextrusion blow-molding: layer (I) of Polypropylene / layer (II) of Tie (L) / layer (III) of EVOH / layer (IV) of tie (L) / layer (V) of Polypropylene, with respective thicknesses of layer (I) to layer (V), in μm , of 390/20/40/20/162.

Table 1

	Ex 1		Ex 2		Ex 3	
	PEm	LLDPE	PEm	LLDPE	PEm	LLDPE
Type of PE						
Density (g/cm ³)	0.87	0.92	0.87	0.92	0.87	0.92
Comonomer	1-octene	1-butene	1-octene	1-butene	1-octene	1-butene
Composition	50%	50%	50%	50%	50%	50%
Degree of grafting	0.9%		0.9%		0.9%	
Grafting monomer	MAH		MAH		MAH	
MFI (g/10 min) 190°C – 2.16 kg	0.7		0.7		0.7	
Proportion of (A)	25%		25%		25%	
Type of PE	E/Me acrylate		E/1-octene		E/Me acrylate	
Density (g/cm ³)	0.943		0.902		0.945	
MFI (g/10 min) 190°C-2.16 kg	8		10		0.5	
Proportion of (B)	75%		75%		75%	
MFI of the blend (A) and (B)	5		4.5		0.5	

Table 2

	CASE 1	CASE 2	CASE 3
	F in N/15 mm	F in N/15 mm	F in N/15 mm
Ex 1	21.8 ⁽¹⁾ and 8.9 ⁽²⁾	-	-
Ex 2	-	21.5 ⁽³⁾ and 18.5 ⁽²⁾	-
Ex 3	-	-	33 ⁽³⁾ and 15-23 ⁽²⁾

⁽¹⁾ failure between layer (II) and layer (III)

⁽²⁾ failure between layer (III) and layer (IV)

⁽³⁾ failure between layer (I) and layer (II)

Table 3

	Ex.2	Ex.3	Comparative Ex.4
Haze (%)	10	13	24